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TECHNICAL REPORT V

Contract N9onr-?5?01

Project Designation NR031-364

... MECHANICS OF SUBSTANCES
... VESSELS FOR LIQUID SODIUM,
POTASSIUM AND NaK.

Mine Safety Appliances Company

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TECHNICAL REPORT V

Contract N9onr-85801

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THE THERMODYNAMICS OF SUBSTANCES USED AS
VESSELS FOR LIQUID SODIUM, POTASSIUM AND NaK.

by

Roy M. Adams

Signed by *R. C. Werner*
R. C. Werner
Project Engineer


Approved by *C. B. Jackson*
C. B. Jackson
Research Supervisor


MINE SAFETY APPLIANCES COMPANY
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## ABSTRACT

Interest in corrosion caused by sodium-potassium alloy has led to the calculation of the free energies of formation of the oxides of metals of possible interest as containers for the alloy or as "getters" for the alloy. The possibility of formation of sodium salts of the acidic metal oxides has also been considered. The data have been assembled into a free energy-temperature chart, from which favorable conditions, if any, for the reaction of a metal with the oxide of another metal may be read at a glance.

### THE THERMODYNAMICS OF SUBSTANCES USED AS
### VESSELS FOR LIQUID SODIUM, POTASSIUM AND NaK.

The possible use of NaK alloy as a heat transfer medium makes important the collection of all possible data on its corrosive properties. Tests in these laboratories with small objects suspended in the hot metal have indicated that addition of oxygen to the liquid alkali metal greatly accelerates the corrosion of other metals. Hence a study of the thermodynamic properties of the oxides of elements of possible use in containers was deemed worthwhile.

A graphical presentation of the results is most advantageous from the standpoint of conciseness and clarity. The large chart at the end of this paper contains plots of the free energies of formation of the various oxides from the elements at the same temperature in the standard state versus the absolute temperature from 300° to 1000°K. This covers the entire liquid ange from the melting point to the boiling point of sodium, potassium and NaK. Where an element formed several oxides, the one having the highest free energy of formation per atom of oxygen was considered.

The possibility of the formation of sodium salts of the more acidic oxides was also considered. The chart contains plots of the free energy of formation of thee such salts. There is a marked paucity of data on such compounds and the plots may be far from accurate. Nevertheless they indicate the possibility of much greater corrosion of elements forming acidic oxides than of those forming solely basic oxides.

The possibility of using an element soluble in sodium to deoxidize the sodium and all other metals contacted (to act as a "getter") was also of interest. The oxides of several such metals are also plotted.

Glasses are affected by the molten metal. Hence the free energies of the reduction of silica and boron trioxide by sodium, the chief components of glasses with high softening temperatures, are also plotted on the chart.

Method of Calculation:

The free energies were calculated in every case from the definitive relationship:

$$(1) \quad \Delta F_f^{\,o} = \Delta H_f^{\,o} - T\Delta S_f^{\,o}$$

where  $\Delta F$  is free energy change

$\Delta H$  is enthalpy (heat content) change

$T$  is temperature in degrees Kelvin

$\Delta S$  is entropy change

$f$  subscript signifies that the thermodynamic property refers to the effect accompanying the formation of the substance from the elements. The superscript $^o$ indicates that the reactants and products are in the standard state (that most common) under a pressure of 1 atmosphere.

Much of the data was taken from reference (1) which, for many of the compounds considered, listed the free energies of formation at 25°C and, for the elements and most of the compounds, the total entropies at 25°C. Most of the higher temperature data came from reference (2), which listed for the elements and compounds the increases in enthalpy $(H_T - H_{298.16})$

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and in entropy $(S_T - S_{298.16})$ above $25°C$. For a few elements and oxides reference (1) part III gives more accurate absolute entropies at high temperatures which were used in preference to Kelley's data[2].

Again at the temperature T:

$$(2) \quad \Delta F^{o}_{f_T} = \Delta H^{o}_{f_T} - T\Delta S^{o}_{f_T}$$

$$(3) \quad \Delta F^{o}_{f_{298.16}} - \Delta H^{o}_{f_{298.16}} - 298.16\Delta S^{o}_{f_{298.16}}$$

subtracting (3) from (2)

$$(4) \quad \Delta F^{o}_{f_T} - \Delta F_{f_{298.16}} = (\Delta H^{o}_{f_T} - \Delta H^{o}_{f_{298.16}}) -$$

$$T\Delta S^{o}_{f_T} - 298.16\Delta S^{o}_{f_{298.16}}$$

Let $\Delta\Delta(f)$ = the increase in the value of the thermodynamic function over that at $25°C$. Then

$$(5) \quad \Delta\Delta F^{o}_{f} = \Delta\Delta H^{o}_{f} - T(\Delta S^{o}_{f_{298.16}} + \Delta\Delta S^{o}_{f}) +$$

$$298.16\Delta S^{o}_{f_{298.16}}$$

rearranging

$$(6) \quad \Delta\Delta F^{o}_{f} = \Delta\Delta H^{o}_{f} - (T - 298.16)\Delta S^{o}_{f_{298.16}} - T\Delta\Delta S^{o}_{f}$$

The increases of enthalpy ($\Delta\Delta H^{o}_{f}$) and entropy ($\Delta\Delta S^{o}_{f}$) for the formation of the compound above those at $25°C$ were then calculated by subtracting these properties for the reactants from the same properties for the products. These values were substituted in equation (6) and the free energy of reaction at the temperature T was then computed by the relationship:

(7) $\Delta F_{f_T} = \Delta F^o_{f_{298.16}} + \Delta\Delta F^o_f$

A sample calculation of the free energies of formation of calcium oxide follows ($Ca + \frac{1}{2}O_2 \longrightarrow CaO$):

### At 25°C (298.16°K)

$\Delta F_f = -144,400$ cal./mole[1]

$S^o$'s[1] in cal./mole-deg.

$CaO_{(s)}9.5$ $\qquad$ $Ca_{(s)}9.95$ $\qquad$ $1/2\ O_{2(g)}24.50$

$\Delta S^o_f = 9.5 - (9.95 + 24.50) = -24.55$

### At 600°K

| | $H_{600} - H_{298.16}$[2] | $S_{600} - S_{298.16}$[2] |
|---|---|---|
| $Ca_{(s)}$ | 2060 | 4.72 |
| $1/2\ O_{2(g)}$ | 1105 | 2.55 |
| Sum | 3165 | 7.27 |
| $CaO_{(s)}$ | 3400 | 7.82 |
| $\Delta\Delta H_f$ | 235 | $\Delta\Delta S_f$ 0.55 |

Again:

(6) $\Delta\Delta F_f = \Delta\Delta H_f - T\Delta\Delta S_f - (T - 298.16)\Delta S^o_f$

$= 235 - 600(0.55) - (302)(-24.55)$

$= +7309$

$\Delta F_{f_{600}} = \Delta F_{f_{298.16}} + \Delta\Delta F_f = -144,400 + 7309$

$= -137,091$ cal.

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Similar calculations were made at 400°, 800° and 1000°K. It was soon noted that $\Delta F_f^0$ varied almost linearly with temperature; so that later calculations were made only for points at 25°C and 600° and 1000°K.

The sources of data for the various oxides (listed alphabetically), together with the reported accuracy of the data follow:

| Oxide | Sources of Data | Accuracy |
|-------|-----------------|----------|
| Aluminum ($Al_2O_3$) | 1, 2 | ± 200 calories |
| Beryllium (BeO) | 1, 2 | ± 1000 calories |
| Boron ($B_2O_3$) | 1, 2 | ± 300 calories |
| Calcium (CaO) | 1, 2 | ± 500 calories |
| Cesium ($Cs_2O$) | 1 | ± 2000 calories |

The entropy of $Cs_2O$ at 25°C was estimated to be 30.5 by the method of Wenner[3] from the entropies of $Cu_2O$, $Ag_2O$, and $Na_2O$. Wenner has shown that the entropies of solids of similar types plotted versus the logarithms of their molecular weights give well defined straight lines. The plots used in this paper are given in the second small chart. No high temperature data was available.

| | | |
|-------|-----------------|----------|
| Chromic oxide ($Cr_2O_3$) | 1, 2 | ± 500 calories |
| Cuprous oxide ($Cu_2O$) | 1, 2 | ± 500 calories |
| Ferrous chromite ($FeCr_2O_4$) | 1, 2 | ± 500 calories |
| Iron oxide (magnetic)($Fe_3O_4$) | 1, 2 | ± 500 calories |

This oxide had a greater free energy of formation per atom of oxygen than either ferrous or ferric.

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Lithium oxide ($Li_2O$)　　　　　1　　　　$\pm$ 2000 calories

The entropy of $Li_2O$ at $25^{\circ}C$ was estimated to be

10.5 in the same manner as that of $Cs_2O$ .

Magnesium oxide (MgO)　　　1, 2　　$\pm$ 500 calories

Manganous oxide (MnO)　　　1, 2　　$\pm$ 500 calories

Molybdenum dioxide ($MoO_2$)　　1　　$\pm$ 1000 calories

No high temperature data was available. $S^{\circ}$ at

$25^{\circ}C$ was estimated to be 18 by the method of Wenner[3]

from the chart on p. 176 for dioxides.

Nickel oxide　　　　　　　　1, 2　　$\pm$ 1000 calories

The increases in entropy of nickel oxide at high

temperatures over the entropy at $25^{\circ}C$ were calculated

by integrating the equation $dS = C_p \dfrac{dT}{T}$ over the

temperature range $298.16^{\circ}K$ to T. The heat capacity

equation used was that given by Seltz[4] to fit the

data of Kapustinskii[5]. The increases in enthalpy

for NiO were also calculated by integrating the equa-

tion $dH = C_p dT$ over the temperature range $298.16^{\circ}K$ to T.

Niobium tetroxide ($Nb_2O_4$)　　　1　　$\pm$ 1500 calories

$S^{\circ}$ at $25^{\circ}C$ was estimated to be 28.5 by the

method of Wenner[3] from the values for $V_2O_4$ and

$Sb_2O_4$  No high temperature data was available

Niobium pentoxide ($Nb_2O_5$)　　1, 2　　$\pm$ 1500 calories

$S^{\circ}$ at $25^{\circ}C$ was estimated to be 32.5 by the method

of Wenner[3] from the values for $V_2O_5$, and $Ta_2O_5$

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Potassium monoxide ($K_2O$)          1          $\pm$ 10,000 calories

    $S^o$ at $25^oC$ was estimated to be 21 by the method
and data used for $Cs_2O$. Kireev[6] gives 26.5 for $S^o$
from additivity calculations based on the alums. This
value was used. The high temperature entropies and
enthalpies of $K_2O$ were taken by subtracting the
values for kyanite ($Al_2SiO_5$) and three moles of
quartz ($SiO_2$) from those of two moles of microcline
($KAlSi_3O_8$). The entropies and enthalpies of many
complex substances are fairly closely equal to the
sum of these properties for their constituents[9,10,12].

Rubidium monoxide ($Rb_2O$)          1          $\pm$ 10,000 calories

    $S^o$ at $25^oC$ was estimated to be 26.5 by the same
method and data used for $Cs_2O$.

Silicon dioxide ($SiO_2$ vitreous) 1, 2     $\pm$     500 calories

Sodium monoxide ($Na_2O$)          1, 2     $\pm$    2000 calories

    The $\Delta H_f^o$ for $Na_2O$ at $25^oC$ was calculated from
Ketchen's value[7] (-44,360 $\pm$ 60 cal./g. atom) for the
heat of solution of sodium in water, Roth's value[8]
for the heat of solution of $Na_2O$ in water, and the
heat of formation of water. The entropies for $Na_2O$
at all temperatures are taken from those of the sodium
silicates and titanates and are subject to the inac-
curacies of the additivity principle;[9] e.g., $S_{298.16}^o$
is given as 17.4 in reference (1). This value is a
mean of values from 16.2 to 18.7 and is based in part
on an inaccurate value for $S_{298.16}^o$ for rutile, but is

the best available. The entropies and heat contents of sodium at high temperatures were taken from reference (13). The slope of the $Na_2O$ free energy-temperature plot is suspiciously steep compared with those of the other oxides.

**Titanium monoxide (TiO)**      1, 2    $\pm$ 1000 calories

$\Delta F_f$ at $25^\circ C$ was estimated to be 142 kcal./mole from the $\Delta F_f$'s of $Ti_3O_5$, $Ti_2O_3$, and $TiO_2$. The increments in $\Delta F_f$ between the successively heavier oxides were almost exactly equal to $\Delta F_f$ for $TiO_2$.

**Vanadium dioxide ($V_2O_2$)**      1    $\pm$ 200 calories

$S^\circ$ at $25^\circ C$ was estimated by the method and data of Wenner[3] (p. 177) to be 11 for the formula VO or 22 for the formula $V_2O_2$. Since no high temperature heat capacity data was available for this oxide, and the data for the trioxide ($V_2O_3$) was available with high accuracy, reference (2) part III, the free energy-temperature relationship for the latter oxide was plotted.

**Zirconium dioxide**      2, 3    $\pm$ 300 calories

## Sodium salts of acidic oxides:

**Sodium meta aluminate ($NaAlO_2$)** 1, 2    $\pm$ 2000 calories

$S^\circ$ at $25^\circ C$ was estimated to be 25, using the method of Wenner[3] and the data for $AgNO_2$ and $AgClO_2^1$. Although these are quite dissimilar compounds, they were the best available for estimation. The high temperature entropies were taken by subtracting three times

the values for the difference in entropies of $Na_2Si_2O_5$ and $Na_2SiO_3$ from the entropies of albite $(NaAlSi_3O_8)$[3]. Since the reaction of interest $(2Na_2O + Al \longrightarrow NaAlO_2 + 3Na$ or $4 Na_2O + 2Al \longrightarrow Na_2O \cdot Al_2O_3 + 6Na)$ involves the reduction of 3 moles of $Na_2O$ by the formation of 2 moles of $NaAlO_2$. The plot is of 2/3 the $\Delta F_f$ of $NaAlO_2$.

Sodium metaborate $(NaBO_2)$  1, 2  $\pm$ 1500 calories

$S^O$ at 25°C was estimated to be 23 by the method used for $NaAlO_2$. This product is chiefly of interest in glass; so the reaction plotted is:

$$3Na + 2B_2O_3 \longrightarrow 3NaBO_2 + B$$
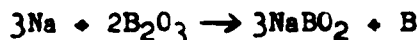
Only the point at 25°C was plotted since no high temperature data on $NaBO_2$ was available.

Sodium chromite $(NaCrO_2)$    $\pm$ 5000 calories

The difference in the $\Delta H_f$'s of $Na_2Cr_2O_4$ and $FeCr_2O_4$ was assumed to be the same as that between $Na_2SiO_3$ and $FeSiO_3$ $\left[ -363 - (-276) = -87 \text{ kcal./mole} \right]$. $\Delta H_{f_{298.16}}$ was given the value $-342 + (-87) = -429$ kcal./mole. By the method of Wenner[3], $S^O_{298.16}$ was estimated to be 47 (for $Na_2Cr_2O_4$) based on the data for $MgCr_2O_4$ and $FeCr_2O_4$, with an addition of 12 for a salt with 2 cations instead of 1. Using the method given for $NaAlO_2$ a value of 27 was estimated for $NaCrO_2$ or 54 for $Na_2Cr_2O_4$. As a mean, a value of 25 for $NaCrO_2$ or 50 for $Na_2Cr_2O_4$ was used. No high temperature data was available, so the slope was plotted parallel to that of $NaAlO_2$. The plot, like that of $NaAlO_2$, is 2/3 $\Delta F_f$ versus T.

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Sodium silicate ($Na_2SiO_3$)      1, 2      $\pm$ 500 calories

The reaction of interest is the effect of sodium on glass.    $4Na + 3SiO_2 \longrightarrow 2Na_2SiO_3 + Si$

## DISCUSSION AND CONCLUSIONS

It is noteworthy that the oxides of all except the most noble elements, e.g. gold and platinum are thermodynamically stable at room temperature. Corrosion control of economically practical structural metals then resolves itself into the problem of protecting the metal from attack by oxygen by the formation of a protective coating or by "gettering or anodizing". The latter can be done by the direct application of a positive electrical potential or by connection with a more electropositive element "a getter". Magnesium is most commonly used for this purpose. Many metals form self-protecting adherent oxide coatings. Chromium forms such a coating. Iron does not; but the addition of ten per cent or more chromium causes the entire oxide coating of the resulting alloy to be adherent. The free energy of formation of chromic oxide indicates that chromium should not be oxidized by sodium oxide at temperatures below 880°Kelvin or 1100°Fahrenheit. But the stainless steels largely used as NaK containers depend on an adherent oxide coating for corrosion protection. The known amphoterism of chromic oxide makes probable its reaction with sodium oxide to form sodium chromite, and it may well be possible that the ferric oxide also reacts to form sodium ferrite. Nickel (II) oxides does not have reported acidic properties. Reaction of sodium oxide with the stainless steel oxide until all the

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chronic and ferric oxide had reacted would explain the observation in this laboratory that the stainless steel absorbs oxygen from sodium oxide for a time and then ceases to absorb it. Since the postulated sodium chromite and sodium ferrite do not appear in the titration analysis, they must be either adherent or insoluble in liquid sodium or potassium.

The fact that sodium chromite formation from sodium oxide and chromium appears to be energetically favored at all temperatures, complicates the picture. ($2Na_2O + Cr \longrightarrow NaCrO_2 + 3Na$). Factors favoring the reverse reaction, however, are the continual presence of a large excess of liquid sodium, the small quantity of chromium available at the steel surface, and the solid state of all the reactants except sodium at operating temperatures.

Two avenues for corrosion prevention seem to be open. The first is use of a metal as a container which forms an adherent basic oxide coating. Nickel fits these requirements admirably. Copper has the desired thermodynamic properties, but is somewhat soluble in hot sodium and the oxide is not adherent. The second means of prevention appears to be "gettering" with calcium or magnesium dissolved in the liquid sodium or potassium. From the thermodynamic properties either of these metals should "getter" any oxide or chromite formation in a sodium-stainless steel system.

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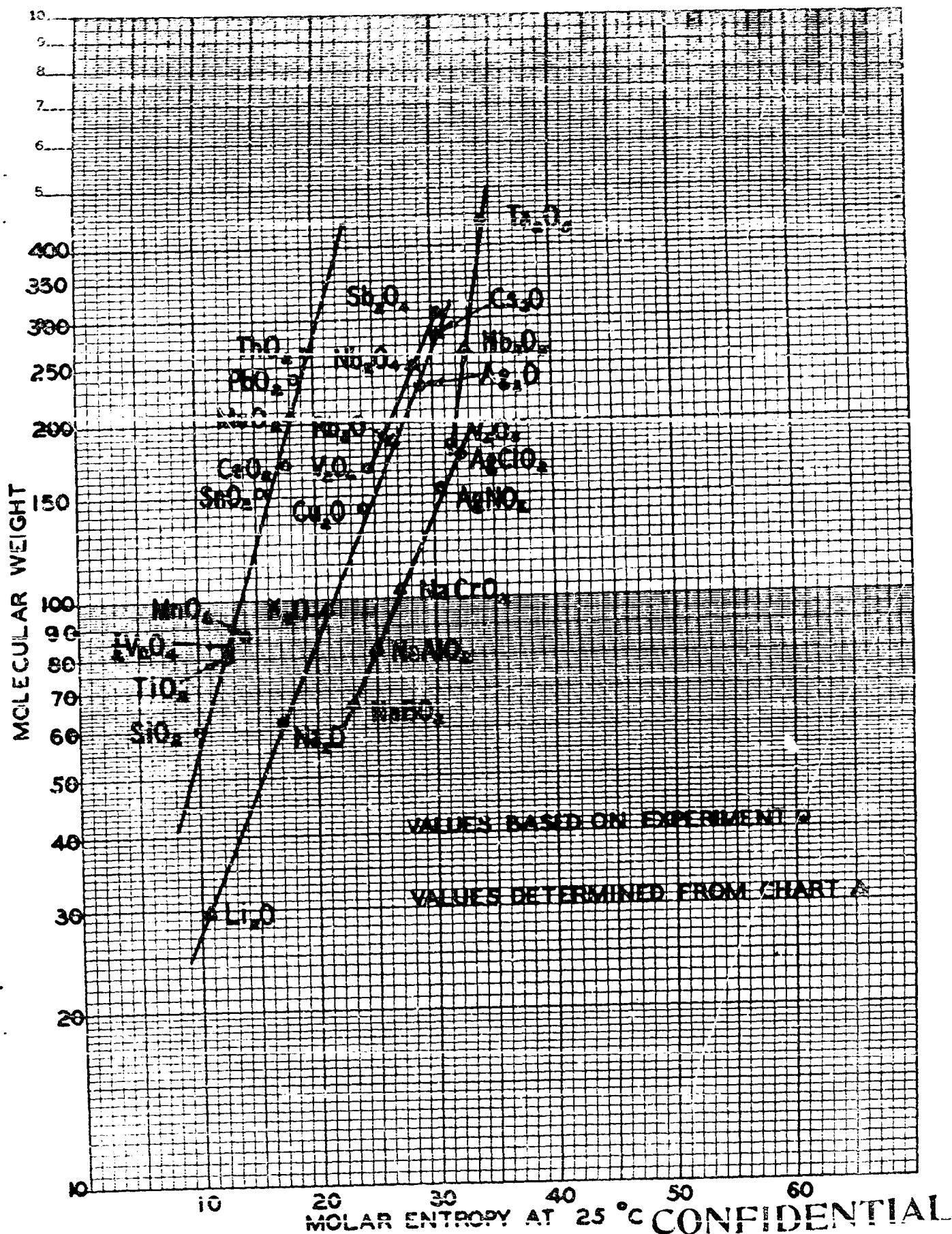
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